



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01B 1/12	A1	(11) International Publication Number: WO 99/24991 (43) International Publication Date: 20 May 1999 (20.05.99)
(21) International Application Number: PCT/GB98/03241 (22) International Filing Date: 30 October 1998 (30.10.98) (30) Priority Data: 9723464.5 7 November 1997 (07.11.97) GB 9801159.6 21 January 1998 (21.01.98) GB (71) Applicant (for all designated States except US): BICC PUBLIC LIMITED COMPANY [GB/GB]; Devonshire House, Mayfair Place, London W1X 5FH (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ADAMS, Phillip, Norman [GB/GB]; 1 Quality Street, High Shincliffe, Durham DH1 2PP (GB). MONKMAN, Andrew, Paul [GB/GB]; Lime Tree House, 50 Front Street, Stanhope, Weardale DL13 2UE (GB). POMFRET, Stephen, John [GB/GB]; 8 Front Street, Frosterley, Bishop Auckland, County Durham DL13 2QJ (GB). (74) Agent: POOLE, Michael, John; BICC Patents & Licensing Dept., Quantum House, Maylands Avenue, Hemel Hempstead, Hertfordshire HP2 7DE (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CONDUCTIVE POLYMER COMPOSITIONS		
(57) Abstract <p>A fluid conductive polymer mixture for use in the preparation of coatings, films and fibres is based on a polyaniline in base form (preferably emeraldine-base form). This is doped with a sulfonic acid having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group and is dispersed in an acid solvent having a pK_a less than 4.5 but substantially higher (more positive) than that of the sulfonic acid. The functional sulfonic acid appears to act as a solvating agent, as well as dopant, and allows the formation of high-solids mixtures in the acid solvents (up to around 15 % w/v compared with a maximum of about 10 % in conventional NMP-based mixtures) from which solvent can be extracted with a competing solvent (e.g. in a wet-spinning process); cold- (and hot-) drawable films and fibres can be obtained. Preferred sulfonic acid is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) or its oligomer and preferred acid solvent dichloroacetic acid. The competing solvent may be acetone, methyl isobutyl ketone or butyl acetate.</p>		

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Conductive Polymer Compositions

This invention relates to conductive polymer compositions and more particularly to fluid compositions based on polyaniline from which conductive fibres, films and coatings can be made.

The emeraldine base form of polyaniline, doped with a sulfonic acid, is now well-established as a useful air-stable conductive polymer (and the leuco base form may also be useful), but conventional fluid compositions only form good films if their solids content is rather small, and even then the films do not draw well. The present invention provides compositions which are capable of use in a wet-spinning process for the manufacture of drawn fibres; they are also useful for the manufacture of drawable films and of coatings by processes in which a competitive solvent is used to achieve solidification faster than is possible by solvent evaporation alone.

The polymer composition in accordance with the invention is the reaction product of:

- (a) a polyaniline in base form;
- (b) an aliphatic sulfonic acid having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group; and
- (c) an acid solvent having a pK_a in aqueous solution at 25°C less than 5 but substantially higher (more positive) than that of the sulfonic acid.

While the invention does not depend on any theory and the applicants do not intend to be bound by theory, it is thought that the sulfonic acid not only acts as a dopant to make the polyaniline conductive but also as a solvating agent to increase the "solubility" of the polymer (the word has been put in inverted commas because the mixtures are sometimes considered to be, at least partly, stable dispersions rather than true (fully solvated) solutions: a homogenising step will usually be required in forming them).

It is also thought that aliphatic sulfonic acids are less liable than the bulky sulfonic acids currently in general use (dodecyl benzene sulfonic acid and camphor-10-sulfonic acid) to inhibit the alignment of polyaniline molecules that is presumably desirable for both drawability and conductivity.

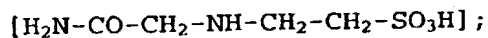
The polyaniline is preferably as free of branching and other defects as possible, and polyanilines of the kind showing only two substantial peaks in their ^{13}C NMR spectra in the leuco base form, in accordance with WO95/23822, are preferred. For making fibres and drawn film, high molecular weight is normally also desirable, but this may not always be so if the mixture is for use in making coatings.

Preferably the polyaniline is in its emeraldine base form; alternatively it is possible to use the leuco base form, though for most applications this will eventually need to be oxidised to the emeraldine form.

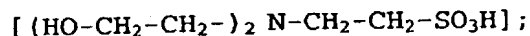
The aliphatic sulfonic acid is preferably wholly free of ring structures (especially aromatic ones), and ideally also free of bulky substituents. Polymerised or polymerisable aliphatic sulfonic acids have the advantage that they are less likely to migrate away from the polyaniline, and may therefore be preferred. High molecular weights are undesirable. Preferred functional groups are carbonyl, amido, amino and hydroxy, especially amido and carbonyl.

Specific aliphatic sulfonic acids that appear to be commercially available and are considered suitable are: 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) $[\text{H}_2\text{C}=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{SO}_3\text{H}]$ (the hydrogenated derivative of this acid can also be used);

N -(2-acetamido)-2-aminoethanesulfonic acid (ACES)



N,N -bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES)



3-(amidinothio)-1-propanesulfonic acid



3-[bis(2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid
 [(HOCH₂-CH₂-)₂N-CH₂-CH(OH)-CH₂SO₃H] and

3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxy-
 1-propanesulfonic acid

5 [HOCH₂-C(CH₃)₂-NH-CH₂-CH(OH)-CH₂SO₃H].

Of these, ACES and most especially AMPSA (and its oligomers)
 are preferred.

The pK_a values of aliphatic sulfonic acids are difficult
 to measure and not readily accessible, but it may be assumed
 10 that they all have pK_a values lower than 1, and in many cases
 below 0.

The proportion of sulfonic acid in the mixture may vary
 in the usual ranges; mostly a proportion in the range from
 0.3 to 1.0 calculated by reference to the number of nitrogen
 15 atoms in the polyaniline will be suitable.

Preferably the acid solvent has a pK_a not greater than 4
 and more especially not greater than 3 or better still 2 or
 even 1.5; preferably it is at least 0.5 units larger (more
 positive) than that of the sulfonic acid. We prefer to use
 20 carboxylic acids that meet these criteria and especially
 those with halogeno- substituents (meaning -Cl, -F or -CN).
 Acid solvents that are liquid at ambient temperature, or not
 far above, are preferred. Most preferred is dichloroacetic
 acid (pK_a = 1.48, melting point 11°C). Other representative
 25 acid solvents and their pK_a's (and melting points) are:

acid solvent	pK _a	m. pt (°C)
bromoacetic acid	2.69	51
chloroacetic acid	2.85	64
cyanoacetic acid	2.45	68
pyruvic acid	2.39	12
2-chloropropionic acid	2.83	#
2-ketobutyric acid	2.5	34
2-chlorobutyric acid	2.86	#
2-oxo-3-methylpentanoic acid	2.3	14

phosphorous acid	1.3	#
formic acid	3.75	8
acrylic acid	4.2	13
acetic acid	4.7	17

melting points not readily available

The mixtures in accordance with the invention may include more than one such acid solvent; they may also include additional solvents (dilutents) and/or host polymers that may become incorporated into the fibres, films or coatings; we prefer that they do not contain lithium chloride (or any inorganic electrolytes). The fluid mixtures in accordance with the invention are green, indicating protonation of the polyaniline.

The invention includes processes for making fibres, films and coatings characterised by the step of removing the acid solvent from the mixtures described by exposing the mixture to the action of a competitive solvent, by which is meant a liquid in which the acid solvent in the mixture is readily soluble but polyaniline is substantially insoluble.

We have found that selected esters and ketones, including in particular acetone, methylisobutyl ketone and butyl acetate are effective and suitable competitive solvents. Water may be too effective for some processes, as it is usually desirable for some of the acid solvent to remain as an aid to subsequent drawing (a plasticiser) and over-rapid solidification may not be conducive to optimum structure; but aqueous solutions of alcohols, ketones and esters may prove usable.

Thus the invention includes

- 1.a process for the manufacture of polyaniline fibre which is a wet-spinning process in which the mixture described is caused to pass through the opening(s) of a spinneret into a bath of competitive solvent and the resulting filament optionally drawn simultaneously or subsequently;
- 2.a process for the manufacture of a polyaniline-coated

substrate in which the mixture described is applied in at least one layer on the surface of the substrate, the layer, or each layer in turn, is exposed to competitive solvent, and the coating is subsequently dried; and

- 5 3. processes for manufacture of polyaniline film in which a coating made as just outlined is freed from the substrate (before or after drying) and optionally uniaxially or biaxially drawn.

Both fibres and films can be cold-drawn (at room
10 temperature) or drawn at elevated temperatures, up to about 150°C. At present we prefer to draw at temperatures in the range from 80 to 120, and more especially 90-100°C for fibres and 100-110°C for films and most especially at the higher end of each of these ranges.

15 EXAMPLES

The polyaniline starting material for these examples is an emeraldine base prepared according to the teaching of WO95/23822 and having a molecular weight (M_p) measured as described in that application of about 150,000 Daltons.

20 Example 1

Polyaniline (3.467g) was ground by a pestle and mortar with AMPSA (4.533g, 57 molecules per hundred nitrogen atoms in the polyaniline) using a glove box with dry nitrogen atmosphere to avoid gelation. The ground mixture was added to
25 dichloroacetic acid (92.0g) to give a mixture with a solids content of 8% by weight (or about 12%w/v, as the acid has a specific gravity of about 1.5). The mixture was homogenised for 10 minutes in a Ultraturrax homogeniser running at 20,000 rpm. The homogenisation/protonation is appreciably
30 exothermic. A portion of the resulting dark green mixture was cast onto a 125 mm diameter polished silicon wafer and dried in an oven at 80°C for about 24 hours. The dried film was peeled from the substrate and found to be 0.202 ± 0.004 mm thick; its electrical conductivity was measured using a 4-

wire probe and found to be 177 ± 6 S/cm. A dumbbell with a bar section 25 mm long and 4.0 mm wide was die-cut from this film and clamped in a stretching rig; it was heated to 110°C and then stretched slowly until the applied force reached 6.0 N. 5 The bar portion of the sample was then 58 mm long (elongation 130%), 0.114 ± 0.004 mm thick and 2.7 mm wide; its longitudinal conductivity was 540 S/cm.

Example 2

Polyaniline (0.632 g) was ground with AMPSA (0.868 g, 60 10 molecules per hundred nitrogen atoms) and added to dichloroacetic acid (28.5 g) and homogenised, using the same procedure as before but under ambient atmosphere as the solids content was only 5%, at which level gelation is not experienced. The solution was cast onto a silicon wafer as 15 before but then immersed in acetone at room temperature for ten minutes to "coagulate" the coating by dissolving part of the dichloroacetic acid. It was dried overnight in the 80°C oven before peeling from the substrate and cutting dumbbells as before. The as-cast film had a conductivity of 20 168 ± 13 S/cm. A sample with an initial cross-section 4 mm by 0.16 mm was stretched at room temperature at a rate of about 1 mm/min without the load exceeding 5.5 N; in a few minutes, an elongation of 115%, retracting reversibly to 100% on removal of the tension, was obtained. The cross-section after 25 stretching was 3 mm by 0.11 mm and longitudinal conductivity 344 ± 35 S/cm. The sample was returned to the stretch rig and held under a tension of 5.5 N at 110°C ; after 10 minutes, the conductivity was found to be 408 ± 40 S/cm, after an hour 459 ± 40 S/cm and after 3 hours 450 ± 40 S/cm. The cross- 30 section at 115% extension was now 2.7 mm by 0.10 mm. It is assumed that residual solvent was lost during this annealing process; there was an appreciable loss of elasticity.

Unstretched samples were also annealed at 110° (for an hour); this was found to produce a steady decline in

conductivity.

Example 3

Polyaniline (1.517 g) was ground with AMPSA (2.083 g, 60 molecules per hundred nitrogen atoms) and then added under nitrogen to dichloroacetic acid (36.4 g) over a 5-minute period while homogenising at 20,000 rpm, generally as in the preceding examples. Homogenising was continued for a further 10 minutes to obtain a 9%-solids mixture (by weight - about 15% w/v). The mixture was transferred immediately, without cooling, to a cylindrical dope-pot 25 mm in diameter having at its bottom end a 140-micrometre filter and a spinneret consisting of a single hole with a diameter of 150 μ m. The pot was removed from the glove box and promptly connected at its top end to a nitrogen gas supply. An electric heating tape was wrapped round the pot to enable it to be brought to and held at a temperature of $50 \pm 5^\circ\text{C}$, and its bottom end was dipped into two litres of cold butyl acetate in a measuring cylinder. The nitrogen pressure in the pot was raised to 0.7 MPa (100 psi) to spin a continuous filament, which was left in the butyl acetate for up to 10 minutes and then dried in air.

The filament was measured with a micrometer and found to have a diameter of 0.30 ± 0.01 mm, and examination with a scanning electron microscope (including examination of a surface formed by fracture at liquid nitrogen temperature) showed it to be smoothly cylindrical and without apparent voids or granules. Longitudinal conductivity of the filament was 70 ± 9 S/cm.

A ten-millimetre length of the filament was stretched at room temperature at a rate of about 10mm/sec, and was thus elongated into a fibre 50 mm long and with a uniform cross-section of 0.10 ± 0.01 mm. Its conductivity was 810 ± 200 S/cm and tensile strength at break about 45 MPa (breaking load 0.4 N).

Example 4

This was substantially the same as Example 3 except that the butyl acetate was replaced by acetone.

The filament diameter (as formed) was 0.26 ± 0.01 mm and
5 its longitudinal conductivity 90 ± 8 S/cm.

A ~~ten-millimetre~~ length of the filament was stretched as
before and thus elongated into a fibre 80 mm long and with a
uniform cross-section of 0.09 ± 0.01 mm. Its conductivity was
then 1014 ± 200 S/cm and tensile strength at break about
10 60 MPa (breaking load 0.41 N).

Example 5

A filament was made by the same procedure as in
Example 4 but in this case the diameter of the filament as
formed (which is very sensitive to precise conditions) was
15 found to be 0.15 mm; its conductivity was still about
90 S/cm.

A 29-mm length of this filament was heated to 90°C and
drawn at a uniform rate to achieve a length of 185 mm over a
ten-minute period. This resulted in a fibre 0.059 ± 0.02 mm
20 in diameter with a conductivity in a longitudinal direction
of 1950 ± 180 S/cm.

Example 6

A solution was made using the same procedure as before with
the same polyaniline emeraldine base, AMPSA and
25 dichloroacetic acid, but in proportions to give 50 molecules
of AMPSA per hundred nitrogen atoms in the polyaniline and a
solids content of only 1.5% by weight and using a 5-minute
homogenisation step followed by centrifuging for 30 minutes
in a typical laboratory centrifuge at 4,500 rpm. Flat glass
30 substrates were coated with enough of this solution to cover
the surface and spun, using a commercial spin coater, at 1700
rpm about an axis normal to the coated surface and through
its centre and while spinning heated to 120°C using an infra-
red heat lamp until dry (around 3 minutes) to obtain a coating

0.07 μ m thick, as measured with an "α-step" profilometer. The film had a conductivity of 60 S/cm, a sheet resistance of 800 ohms per square and an optical transmission of 95% at 550 nm.

CLAIMS

- 1 A fluid conductive polymer mixture for use in the preparation of coatings, films and fibres which is the reaction product of:
- 5 (a) a polyaniline in base form;
- (b) a sulfonic acid having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group; and
- (c) an acid solvent having a pK_a less than 5 but
- 10 substantially higher (more positive) than that of the sulfonic acid.
- 2 A fluid mixture as claimed in claim 1 in which the polyaniline is of the kind showing only two substantial peaks in the ^{13}C NMR spectrum of its leuco base form.
- 15 3 A fluid mixture as claimed in claim 1 or claim 2 in which the polyaniline is in its emeraldine base form.
- 4 A fluid mixture as claimed in any one of claims 1-3 in which the aliphatic sulfonic acid is wholly free of ring structures.
- 20 5 A fluid mixture as claimed in any one of claims 1-4 in which the aliphatic sulfonic acid is polymerisable.
- 6 A fluid mixture as claimed in any one of claims 1-5 in which the said functional groups in the sulfonic acid are selected from the group consisting of carbonyl, amido, amino
- 25 and hydroxy.
- 7 A fluid mixture as claimed in any one of claims 1-5 in which the said functional groups in the sulfonic acid are selected amido or carbonyl.
- 8 A fluid mixture as claimed in claim 1 or claim 2 in
- 30 which the aliphatic sulfonic acid is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA).
- 9 A fluid mixture as claimed in claim 1 or claim 2 in which the aliphatic sulfonic acid is selected from:
- N*-(2-acetamido)-2-aminoethanesulfonic acid (ACES);
- 35 *N,N*-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (BES);

3-(amidinothio)-1-propanesulfonic acid; 3-[bis(2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid; 3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid; and the hydrogenated derivative of
5 AMPSA.

- 10 A fluid mixture as claimed in any one of claims 1-9 in which the proportion of sulfonic acid in the mixture is in the range from 0.3 to 1.0 calculated by reference to the number of nitrogen atoms in the polyaniline.
- 11 A fluid mixture as claimed in any one of claims 1-10 in which the acid solvent has a pK_a not greater than 4.
- 12 A fluid mixture as claimed in any one of claims 1-10 in which the acid solvent has a pK_a not greater than 3.
- 13 A fluid mixture as claimed in any one of claims 1-10 in
15 which the acid solvent has a pK_a not greater than 2.
- 14 A fluid mixture as claimed in any one of claims 1-10 in which the acid solvent has a pK_a not greater than 1.5.
- 15 A fluid mixture as claimed in any one of claims 1-14 in which the acid solvent has a pK_a at least 0.5 units larger
20 (more positive) than that of the sulfonic acid.
- 16 A fluid mixture as claimed in any one of claims 1-15 in which the acid solvent is a carboxylic acid.
- 17 A fluid mixture as claimed in any one of claims 1-15 in which the acid solvent is a carboxylic acid with halogeno-
25 substituents (-Cl, -F or -CN).
- 18 A fluid mixture as claimed in any one of claims 1-15 in which the acid solvent is dichloroacetic acid.
- 19 A fluid mixture as claimed in any one of claims 1-15 in which the acid solvent is selected from trichloroacetic acid,
30 bromoacetic acid, chloroacetic acid, cyanoacetic acid, pyruvic acid, 2-chloropropionic acid, 2-ketobutyric acid, 2-chlorobutyric acid, 2-oxo-3-methylpentanoic acid, phosphorous acid, formic acid, acrylic acid and acetic acid.
- 20 A process for making conductive polymer fibre, film or
35 coating including preparing a fluid mixture as claimed in any

one of claims 1-19 and removing acid solvent by exposing the mixture to the action of a competitive solvent.

21 A process for the manufacture of polyaniline fibre which is a wet-spinning process comprising preparing a fluid
5 mixture as claimed in any one of claims 1-19, and causing it to pass through the opening(s) of a spinneret into a bath of competitive solvent.

22 A process as claimed in claim 21 comprising
10 simultaneously or subsequently drawing the resulting filament.

23 A process as claimed in claim 22 in which the filament is drawn at room temperature.

24 A process as claimed in claim 22 in which the filament is drawn at a temperature in the range 90-100°C.

15 25 A process as claimed in any one of claims 20-24 in which the competitive solvent is acetone, methylisobutyl ketone or butyl acetate.

26 A process for the manufacture of a polyaniline-coated substrate comprising preparing a fluid mixture as claimed in
20 any one of claims 1-19, applying it in at least one layer on the surface of the substrate, exposing the layer, or each layer in turn, to a competitive solvent, and subsequently drying the coating.

27 A process for the manufacture of a polyaniline film
25 comprising preparing a mixture as claimed in any one of claims 1-19, applying it in at least one layer on the surface of the substrate, exposing the layer, or each layer in turn, to a competitive solvent, freeing the coating from the substrate and then drying it.

30 28 A process for the manufacture of a polyaniline film comprising preparing a mixture as claimed in any one of claims 1-19, applying it in at least one layer on the surface of the substrate, exposing the layer, or each layer in turn, to a competitive solvent, subsequently drying the coating,
35 and freeing it from the substrate.

29 A process as claimed in claim 27 or claim 28 in which the competitive solvent is acetone, methylisobutyl ketone or butyl acetate.

30 A process as claimed in any one of claims 27-29 in which
s the film is uniaxially or biaxially drawn.

31 A process as claimed in claim 30 in which the film is drawn at room temperature.

32 A process as claimed in claim 31 in which the film is drawn at a temperature in the range 100-110°C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03241

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CAO YONG ET AL: "Effect of solvents and co-solvents on the processibility of polyaniline: I. solubility and conductivity studies" PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON SCIENCE AND TECHNOLOGY OF SYNTHETIC METALS (ICSM'94). PART 1; SEOUL, SOUTH KOREA JUL 24-29 1994, vol. 69, no. 1-3 part 1, 24 July 1994, pages 187-190, XP002091335 Synth Met; Synthetic Metals; Polymers Mar 1 1995 Elsevier Science S.A., Lausanne, Switzerland	1,3,6,7, 10-19,26
A	see page 189, column 1, paragraph 4; table 1 --- -/-	20-25, 27-32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Form PCT/ISA/210 (patent family annex) (July 1992)